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(54) Title: PROCESS FOR MOLDING ARTICLES HAVING A DURABLE HIGH STRENGTH HIGH GLOSS GEL COAT  (57) Abstract  Fiber-reinforced plastic articles having a gel coat with high initial gloss and extended gloss retention are made by a process comprising the steps of: A) spreading a peroxide-curable gel coat composition over the surface of a mold that is in negative relief of the article to be molded; B) at least partially curing the gel coat composition; C) spreading a fiber reinforced, plastic compo- sition over the at least partially cured gel coat composition to form a laminate; and D, curing the laminate to form the fiber-rein- forced plastic article.		

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## PROCESS FOR MOLDING ARTICLES HAVING A DURABLE HIGH STRENGTH HIGH GLOSS GEL COAT.

This invention relates to coated, molded articles. In one aspect, this invention relates to coated, molded articles comprising a plastic laminated to a gel coat which, upon cure, exhibits a high quality gloss, while in another aspect, this invention relates to a process for making such articles.

Coated, molded articles, often fiber-reinforced, are typically made by spreading over the surface of a mold having a surface corresponding to the article in negative relief, a gel coat composition which upon cure, becomes the first barrier against the environment. The gel coat is spread across the surface of the mold by any one of a number of conventional techniques, e.g. brushing, hand lay-up, spraying, etc., and it is usually applied relatively thick, e.g. 0.5 to 0.8 mm, to maximize its weather and wear resistance and if the molded article is fiber-reinforced, to help in hiding the fiber reinforcement pattern which could otherwise show through the gel coat due to the inherent resin shrinkage that occurs around the fibers during cure. This effect is commonly termed "fiber print through" in the fiber-reinforced plastic industry.

After the gel coat is applied to the surface of the mold, it is at least partially cured. The plastic is then applied to the partially or fully cured gel coat, again by any one of a number of conventional techniques, and the resulting laminate structure cured. The cure can be promoted through the use of elevated temperature and pressure.

In addition to affording weather and wear resistance to the molded article, the gel coat also imparts cosmetic properties to the article. In many applications, particularly consumer applications such as automobile parts, appliance facie, etc., a high initial gloss and extended gloss retention are very desirable properties for the molded article. Present gel coats often exhibit a high gloss upon cure, but lose this gloss over time due to a variety of environmental factors, e.g. sunlight, heat, cold, water, corrosive chemicals, etc., long before the end of the useful life of the article. Moreover, loss of gloss is often accompanied by the appearance of surface defects such

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as cracks, coarseness, blisters, etc., and these are often indicative of structural deterioration of the molded article itself.

The high quality gel coats presently in use are isophthalic acid/neopentyl glycol (IPE/NPG) based unsaturated polyesters diluted in styrene monomer, but these compositions are rather soft materials of overall low chemical resistance and limited outdoor durability. The marine industry in particular is in need of an improved gel coat for boat hulls because IPA/NPG gel coats can fade and chalk before the boat is sold from the marine yard and actually placed in the water.

Other gel coats presently in use include epoxy, urethane and vinyl ester gel coats, particularly when greater flexibility and water resistance are desired. However, these materials also tend to fade and lose their gloss quickly, and they usually require higher curing temperatures or are much more difficult to use than the more commonly available unsaturated polyester products. In addition, these compositions are difficult to formulate into gel coats having desirable physical properties, in-mold curing times and handling properties without the use of more than a nominal amount of styrene or similar volatile monomer as a reactive diluent. Moreover, these diluents are the subject of numerous federal, state and local regulations and as such, manufacturers of molded plastic articles prefer to use gel coat compositions that contain minimal styrene or like volatile monomers.

Gel coats can, of course, be applied to the plastic after it has been at least partially cured and while these post-cure applied gel coats improve the water resistance, initial gloss and gloss retention of the plastic, they themselves often have a low initial gloss and poor gloss retention relative to pre-cure applied gel coats.

Of course, various coatings can be applied to the demolded article to improve the wear resistance, initial gloss and gloss retention of the structure, but not only do these coatings require another costly application step, but they also suffer from poor adhesion to the gel coat, particularly if traces of mold release remain on the surface of the gel coat. Moreover, unlike the gel coat compositions themselves, these coatings are normally low solids

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compositions that are prone to comestically undesirable rheological surface defects such as brush marks, orange peel, craters, ripples, fish eyes, and the like.

According to this invention, plastic articles having a high  
5 initial gloss and extended retention are made by a process comprising the steps of :

- A. Providing a mold having a surface corresponding to the article in negative relief ;
- B. Spreading over at least a portion of the surface of the said mold a  
10 peroxide-curable gel coat composition comprising :
  1. An  $\alpha$ ,  $\beta$ -ethylenically unsaturated oligomer selected from the group consisting of unsaturated polyesters, and acrylated and methacrylated urethanes, epoxies, polyesters and polyethers ;
  2. A curing amount of a polyallylic crosslinker-initiator ; and
  - 15 3. A cure-rate promoting amount of a metallic salt drier ;
- C. At least partially curing the gel coat composition ;
- D. Spreading at least a partially uncured, plastic composition over the at least partially cured gel coat composition to form a laminate ;
- 20 E. Curing the laminate to form the plastic article ; and
- F. Removing the plastic article from the mold.

In one embodiment of this invention, the oligomer is diluted with an  $\alpha$ ,  $\beta$ -ethylenically unsaturated monomer while in another embodiment, the crosslinker-initiator is used in combination with a  
25 co-initiator. Other additives, e.g. reinforcing fiber, leveling agents, pigments, cure promoters other than metallic salt driers, etc., can also be present.

The molded, plastic articles made by the process of this invention exhibit gel coats that not only have very desirable gloss and  
30 gloss retention properties, but gel coats that exhibit excellent outdoor durability, hardness, toughness and good handling properties during the molding process. Moreover, the gel coat compositions can be formulated with little, if any, styrene or other volatile reactive diluents with emission properties similar to styrene.

35 Illustrative  $\alpha$ ,  $\beta$ -ethylenically unsaturated oligomers which cure by thermally induced free radical polymerization include unsaturated

polyesters, urethane acrylates, urethane methacrylates, epoxy acrylates, epoxy methacrylates, polyester acrylates, polyester methacrylates, polyether acrylates and polyether methacrylates.

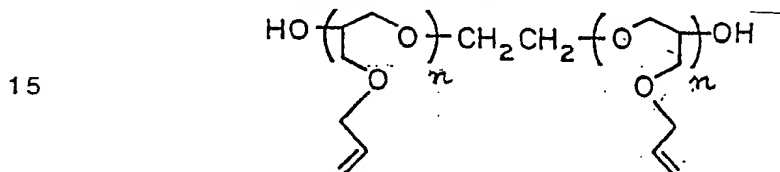
- Epoxy acrylates and methacrylates include the reaction products of diepoxides with acrylic or methacrylic acid, for example the reaction product of methacrylic or acrylic acid with the diglycidyl ether of bisphenol A. Urethane acrylates and methacrylates include the reaction products of hydroxy alkyl acrylates and methacrylates with organic isocyanates, for example, the reaction product of isophorone diisocyanate with hydroxy ethyl methacrylate. Other urethane acrylates include the reaction products prepared by combining an organic diisocyanate, hydroxy alkyl acrylate or methacrylate with a polyol such as propylene glycol, a glycol diester, or a polycaprolactone diol or triol. Unsaturated polyesters include the reaction products of  $\alpha$ ,  $\beta$  unsaturated dicarboxylic acids or anhydrides and a polyhydric alcohol, for example the reaction product of maleic anhydride with propylene glycol. Polyester acrylates and methacrylates include the reaction products of saturated polyester polyols with acrylic or methacrylic acid, for example the reaction product of esters of adipic acid and neopentyl glycol with acrylic acid. Polyether acrylates and methacrylates include the reaction products of glycol ethers and acrylic or methacrylic acid, for example the reaction product of dipentaerythritol and acrylic acid.

- The unsaturated oligomers used in the practice of this invention are selected for optimum properties in the final product. For outdoor weather resistant or abrasion resistant characteristics, urethane acrylate and methacrylate based on aliphatic isocyanates resins are optimum. For chemical resistance, epoxy acrylates and methacrylates are optimum.

- In one embodiment of this invention, the unsaturated oligomers are diluted with one or more  $\alpha$ ,  $\beta$ -ethylenically unsaturated monomers which crosslink with the oligomers through thermally induced free radical polymerization. Illustrative monomers include the mono-, di- and trifunctional acrylic and methacrylic esters, N-vinyl-2-pyrrolidone, N-methylol acrylamide, the hydroxy

alkyl esters of acrylic and methacrylic acid, and aromatic vinyl and divinyl compounds. Unsaturated monomers with relatively low volatility under process conditions, such as the polyfunctional acrylic and methacrylic esters, are preferred.

- 5 Representative of the polyallylic crosslinker-initiators that can be used in the practice of this invention are polyester resins based on trimethylolpropane mono- or diallyl ethers and polyallylglycidyl ether alcohol resins. Those crosslinker-initiators that function both as latent initiators for low temperature free radical polymerization of  
10 the oligomers and, if present, monomers, and as a multifunctional crosslinker are the preferred crosslinker-initiators. Polyallylic ethers having the general formula



wherein n is an integer from 2 to 10 are representative of these preferred crosslinker-initiators.

- 20 Any metallic salt drier that will promote or accelerate the rate of cure of the  $\alpha$ ,  $\beta$ -ethylenically unsaturated oligomer, crosslinker-initiator and, if present, monomer, can be used in the practice of this invention. Typical of these driers are salts of metals with a valence of two or more and unsaturated organic acids.  
25 Representative metals include cobalt, magnesium, cerium, lead, chromium, iron, nickel, uranium and zinc. Representative acids include linoleates, naphthenates, octoates, and resinates. Preferred metallic salt driers include the octoates, naphthenates and neodecanoates of cobalt, manganese, vanadium, potassium, zinc and  
30 copper. Especially preferred metallic salt driers are the cobalt-based driers such as cobalt octoate, cobalt naphthenate and the organo-complexes of cobalt and potassium.

- The rate of cure, especially at relatively low temperatures, e.g. 21° to 38°C, can be further accelerated through the use of one or  
35 more co-initiators. These co-initiators are typically non-polyallylic peroxides, and include any of the common peroxides such as benzoyl

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peroxide ; dialkyl or aralkyl peroxides such as di-t-butyl peroxide, dicumyl peroxide, cumylbutyl peroxide, 1,1-di-t-butylperoxy-3,5,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di-t-butylperoxy hexane and bis ( $\alpha$ -t-butylperoxy isopropylbenzene) ; peroxyesters such as t-butylperoxy pivalate, t-butyl peroctoate, t-butyl perbenzoate, 2,5-dimethylhexyl-2,5-di (perbenzoate), dialkylperoxymonocarbonates and peroxydicarbonates ; hydroperoxides such as t-butyl hydroperoxide, p-methane hydroperoxide, pentane hydroperoxide and cumene hydroperoxide ; and ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide.

The amount of unsaturated oligomer and, if present, monomer present in the gel coat composition can vary to convenience with the exact amounts in any given formulation a function of the physical and chemical properties desired in the cured coating. Typically, the oligomer or if monomer is present, then the oligomer and monomer mixture, comprises at least about weight 65 %, based on the precured weight of the gel coat composition, of the composition, preferably at least about weight 75 %. The maximum amount of these materials in the composition usually does not exceed about 95 wt %, preferably about 90 wt %. If an oligomer-monomer mixture is used in the practice of this invention, then the amount of monomer present in the mixture can vary to convenience but typically it does not exceed about 30 wt %, preferably about 20 wt %, of the mixture.

At least a curing amount (i.e. an amount sufficient to cure or crosslink the oligomer and, if present, monomer into a durable, high quality gel coat) of polyallylic crosslinker-initiator is present in the precured gel coat composition of this invention and although this amount can vary, it usually does not exceed about 35 wt %, preferably about 25 wt %, of the composition. Typically, the minimum amount of this crosslinker-initiator present is in excess of about 5 wt %, preferably in excess of about 10 wt %, of the composition. If a co-initiator is present, then it is typically present in an amount between about 1 and 10 wt %, based on the precured weight of the gel coat composition.

At least a cure-rate promoting amount (i.e. an amount that promotes the rate of cure of the oligomer, polyallylic crosslinker-



initiator and if present, monomer) of the metallic salt drier is present in the precured gel coat compositions of this invention. This amount, like the amount of crosslinker-initiator, can vary, but this amount, based on the wt % of metal in the drier (usually between  
5 about 4 and 15 wt %), typically is in excess of 0.005 wt %, preferably in excess of 0.01 wt %, and more preferably in excess of 0.03 wt %. Typically, this amount is not in excess of about 0.08 wt %, preferably not in excess of about 0.05 wt %, and more preferably not in excess of about 0.04 wt %.

10 The precured gel coat compositions can contain one or more additives to facilitate processing or to impart some desirable feature or property to the molded plastic article. For example, solvents may be added to reduce the viscosity of the precured gel coat composite, which in turn makes easier to apply the composition to the mold.  
15 Preferably these solvents are reactive diluents, e.g. one or more of the  $\alpha$ ,  $\beta$ -ethylenically unsaturated monomers, that are relatively nonvolatile at curing conditions. If the solvent is a nonreactive diluent, then it must be removed prior to or during the cure process. Other additives, such as fluoroocarbons, silicones, pigments,  
20 cellulose acetate butyrate, and the like, may also be present to control flow, leveling, color, thixotropy, and the like. Cure promoters in addition to the metallic salt driers can also be present, such as N,N-dimethyl-p-toluidine, N,N-dimethyl aniline, N,N-diethyl aniline, 2,4-pentanedione and N,N-dimethyl acetaniline.

25 In the process of this invention for molding a laminated plastic article, a mold surface corresponding to the article in negative relief is at least partially, preferably completely, covered with the peroxide-curable gel coat composition. Typically, this composition is formulated from its constituent components just prior to its  
30 application to the mold surface. The oligomer and metallic salt drier are blended with one another prior to the addition of the polyallylic crosslinker-initiator. If an  $\alpha$ ,  $\beta$ -ethylenically unsaturated monomer is present, then it is blended with the oligomer and metallic salt drier prior to the addition of the polyallylic crosslinker-initiator or, if  
35 present, a co-initiator. If a co-initiator is present, then it is blended

with the polyallylic crosslinker-initiator prior to the crosslinker-initiator being blended with the oligomer and metallic salt drier.

The gel coat composition is applied as a thick coat, relative to the thickness of a coat of paint, but usually less than 1 mm, preferably less than 0.5 mm. The composition is then at least partially cured, either at ambient conditions, e.g. 20° to 40°C and atmospheric pressure, or at an elevated temperature, e.g. at a temperature in the range of about 40° to 95°C. "Partially cured" here means that the gel coat composition is sufficiently cured to retain its shape without significant distortion, while still on the mold surface, during the application of at least a partially uncured plastic to its exposed surface. The cure time will vary with the nature of the gel coat composition, curing conditions, thickness of the gel coat, and a host of other factors but typical cure times for many of the commercially available unsaturated oligomers, in combination with a polyallylglycidyl ether crosslinker-initiator are in the range of about 240 to 300 minutes at about 20° to 27°C, and about 20 to 45 minutes at about 65° to 70°C, for a coat of less than 1 mm in thickness. The gel coat composition can be applied to the mold surface in any convenient manner, e.g. hand lay-up, spraying, dipping, brushing, rolling, etc. The mold contact surfaces may be made of any conventional materials such as glass, reinforced polyesters, epoxies, steel, aluminium, and the like.

After the gel coat composition has at least partially cured, preferably completely cured, the at least partially uncured, preferably essentially completely uncured, plastic is applied to the exposed surface of the gel coat. "Partially uncured" here means that the plastic is sufficiently fluid to permit its application to the exposed surface of the at least partially cured gel coat composition by one or more conventional means, e.g. spraying, brushing, injection, etc. The nature of the plastic can vary to convenience, but typical plastics include unsaturated polyesters, phenolics, epoxies, urethanes, etc.

The mold may be an open mold or a matched mold, i.e. a two component mold comprising a female mold surface and a male mold surface that when joined, define a volume with the shape of the

desired molded product. If an open mold, then once the plastic has been applied to the exposed surface of the at least partially cured gel coat composition, then it is allowed to cure under ambient conditions or more commonly, placed in an oven to promote cure. If  
5 a matched mold, then once the gel coat is at least partially cured the mold is closed and the plastic injected under pressure into the mold to completely fill the volume formed by the two mated mold surfaces. The mold is retained in this closed position for a sufficient period of time to allow the molded article to complete cure, typically  
10 at an elevated temperature and pressure, and to allow a strong bond to form between the gel coat and the plastic. The mold is then opened, and the molded article removed. Mold release agent can be used with both open and matched molds as desired.

In one embodiment of this invention, the plastic is fiber-  
15 reinforced. The reinforcing fiber can vary to convenience, and typical reinforcing fibers include glass, polyethylene, metal, ceramic and the like. While the fiber can be admixed with the plastic prior to the application of the plastic to the at least partially cured gel coat composition, more commonly the fiber is applied to the at least  
20 partially cured gel coat composition as a preform. Typically, a matched mold is used. The preform is inserted over the at least partially cured gel coat composition, the mold is closed, and the plastic injected. Upon cure, a fiber-reinforced plastic article is formed.

25 The gel coats of the laminated, fiber-reinforced plastic molded articles of this invention exhibit high physical strenghts, a very desirable high initial gloss and an excellent gloss retention in addition to such other desirable properties of providing protection to the underlying fiber-reinforced plastic against heat, cold, sunlight,  
30 water, corrosive chemicals, and the like. Moreover, these desirable properties are obtained with coatings that are thin relative to the thickness of conventional coatings, e.g. those based on isophthalic acid and neopentyl glycol.

The following examples are illustrative of certain embodiments  
35 of this invention. Unless indicated to the contrary, all parts and percentages are by weight.

Example 1Preparation of Urethane Acrylate Oligomer

Into a reaction flask equipped with an agitator, liquid additional funnel, thermometer and inlet tube for the introduction of dry air for maintaining an anhydrous atmosphere were placed 1453 grams of isophoronediiisocyanate, 4 grams of dibutyl tin dilaurate and 1 gram of toluene hydroquinone. To this solution was slowly added 760 grams of 2-hydroxyethylacrylate over a 1 hour period while maintaining a reaction temperature of between 30° and 40°C. After 10 agitating the reaction mixture in this temperature range for 1 hour, the temperature was raised to about 70°C and 600 grams of ethyltriglycolmethacrylate and 1177 grams of 540 molecular weight caprolactone triol were added. The resulting mixture was agitated and held in a temperature range of 70° to 80°C until infrared analysis 15 indicated disappearance of the -NCO absorption peak (3 hours).

Preparation and testing of a Gel Coat

A gel coat composition was prepared by combining a pigment grind comprised of 31.5 grams of the urethane acrylate oligomer prepared above, 8.6 grams of propylene glycol monomethyl ether 20 acetate, 12.9 grams of aromatic solvent, 43.1 grams of titanium dioxide (rutile grade R902 from the E.I. Du Pont de Nemours, Co.), 2.2 grams of acetoacetoxyethyl methacrylate, 0.28 grams of cobalt naphthenate, 0.004 grams of methyl ethyl ketoxime, pigment grinding aides, flow additives with 8.6 grams of Santolink® XI-100 25 (sold by MONSANTO Company) as a crosslinker-initiator, and 0.43 grams of cumene hydroperoxide.

The resulting peroxide-curable gel coat composition was drawn down on a waxed glass plate at a wet film thickness of 10 mils (dry film thickness of 0.18 mm). After curing for 60 minutes at 75°C, 30 the gel coat surface in contact with the glass plate was tack free and the surface exposed to air had a slight tackiness. At this point a peroxide catalyzed unsaturated polyester laminating resin was applied onto the gel coat and allowed to harden for 12 hours before removing the composite from the glass plate. The resulting white gel 35 coated panel had an initial gloss of 89 on the 60 degree Gardner scale and 76 on the 20 degree scale.

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- 5 The panel was then placed in an ultra-violet accelerated weathering unit alongside a panel of white 0.5 mm thick high performance conventional isophthalic acid/neopentyl glycol unsaturated polyester gel coated laminate. Similar panels of each were also placed on a 45 degree exposure rack in south Florida. The gloss of the exposed panels was periodically measured. The results of both the ultra-violet accelerated weathering unit and the south Florida exposure tests are reported in Table I.

Table I

QUV EXPOSURE (light hours)	0	305	507	811	1319
60 GLOSS					
Urethane Acrylate Based					
Gel Coat	89	75	69	47	46
Conventional Gel Coat	94	15	7	0	0
20 GLOSS					
Urethane Acrylate Based					
Gel Coat	76	52	30	10	9
Conventional Gel Coat	81	2	0	0	0
FLORIDA EXPOSURE (months)	0	3	6	9	12
60 GLOSS					
Urethane Acrylate Based					
Gel Coat	91	91	93		
Conventional Gel Coat	82	89	75	55	49
20 GLOSS					
Urethane Acrylate Based					
Gel Coat	81	80	82		
Conventional Gel Coat	75	56	36		

Example 2Preparation of the Urethane Methacrylate Oligomer

In the apparatus described in Example 1 were placed 1616 grams of isophoronediiisocyanate, 5 grams of dibutyltindilaurate, and 1 gram of toluhydroquinone. To this solution was slowly added 948 grams of 2-hydroxyethylmethacrylate over a period while maintaining a reaction temperature in the range of 30° to 40°C. After agitating the reaction mixture in this temperature range for 1 hour,

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the temperature was raised to 70°C and 500 grams of 2-ethylhexylmethacrylate and 1921 grams of a 530 molecular weight caprolactone diol were added. The resulting mixture was agitated and heated in a temperature range of 70° to 80°C until infrared  
 5 analysis indicated the disappearance of the -NCO absorption peak (3 hours).

#### Preparation and Testing of a Gel Coat

The urethane methacrylate prepared above was substituted for the urethane acrylate in the formulation and procedure of Example  
 10 1.

The resulting white gel coat was subject to the same accelerated weathering and outdoor Florida exposure tests as the panels of example 1. Results are reported in table II below.

Table II

QUV EXPOSURE (light hours)	0	115	478	669	1051	1437
60 GLOSS						
Urethane Acrylate Based						
Gel Coat	84	86	46	32	36	30
20 GLOSS						
Urethane Acrylate Based						
Gel Coat	65	44	16	7	20	12
FLORIDA EXPOSURE (months)	0	3	6	9	12	
60 GLOSS						
Urethane Acrylate Based						
Gel Coat	90	89	93			
20 GLOSS						
Urethane Acrylate Based						
Gel Coat	57	58	54			

#### Example 3

##### Preparation of an Unsaturated Polyester Oligomer

Into a reaction flask equipped with an agitator, nitrogen gas inlet tube, packed column, and condensor were placed 1129 of grams neopentyl glycol and 1564 grams of 1,4 cyclohexane dimethanol. This mixture was heated to 94°C at which time 1082 grams isophthalic acid and 0.7 gram butyl stannic acid were

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introduced. The reaction mixture was heated to 180°C and then gradually to 220°C while removing the esterification water.

- When an acid value of 0.8 was reached the reaction mixture was cooled to 177°C and 958 grams of maleic anhydride and 0.4 grams of monotertiarybutyl hydroquinone were added. This reaction mixture was heated to 204°C and held at this temperature until the acid value reached 29. Xylene (100 grams) was then added for refluxing and the temperature was held at 204°C until the acid value was reduced to 5. The resulting resin was cooled, and additional xylene was added to give a 80 % resin solution.

#### Preparation and Testing of a Gel Coat

The polyester prepared above was substituted for the urethane acrylate in the formulation and procedure of Example 1.

- The resulting white gel coat was subjected to the same accelerated weathering and outdoor Florida exposure as the gel coats of Examples 1 and 2. Results are reported in Table III below.

Table III

QUV EXPOSURE (light hours)	0	304	478	669	1051	1437
60 GLOSS						
Urethane Acrylate Based						
Gel Coat	90	84	86	73	51	4
20 GLOSS						
Urethane Acrylate Based						
Gel Coat	71	55	50	10	6	5
FLORIDA EXPOSURE (months)	0	3	6	9	12	
60 GLOSS						
Urethane Acrylate Based						
Gel Coat	84	86	88			
20 GLOSS						
Urethane Acrylate Based						
Gel Coat	65	67	72			

#### Example 4

A gel coat composition was prepared by combining a pigment grind comprised of 24.4 grams of the urethane acrylate of Example 1, 6.1 grams of the reaction product of one mole of isophoronediiisocyanate and 2 moles of hydroxyethylmethacrylate,

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11.3 grams of rutile grade titanium dioxide, 0.3 grams of cobalt naphthenate, 0.08 grams of methyl ethyl ketoxime, 1.9 grams of acetoacetoxyethylmethacrylate, pigment grinding aids, and flow control additives with 0.5 grams of the mono-adduct of  
5 hydroxylethylmethacrylate and phthalic anhydride, 9.5 grams Santolink® XI-100, and 0.7 grams of cumene hydroperoxide.

A 0.13 mm thick film of the resulting peroxide-curable gel coat composition was drawn down on a waxed glass plate. After curing for 30 minutes at 75°C, the gel coat surface which had been  
10 in contact with the glass plate was tack free and the surface which had been in contact with the atmosphere had a very slight tack. Then an acid-catalyzed phenolic molding resin filled with 2 layers of one and one half ounce continuous strand glass mat was laminated to the gel coat and allowed to cure for one hour at 65°C.

15 The resulting gel coated panel had a "F" pencil hardness on the gel coated side and gloss readings of 87 on the 60 degree Gardner scale and 77 on the 20 degree Gardner scale. There was no gel coat adhesion loss when the panel was subjected to crosshatching and tape pulling with No. 600 Scotch Brand adhesive  
20 tape.

When the gel coat composition was post applied to a cured phenolic panel, the gel coat showed 50 % adhesion failure and had gloss readings of 78 and 42, respectively, on the 60 and 20 degree Gardner scales.

25 Example 5

The gel coat composition of Example 4 was modified by substituting 14.8 grams of dipentaerythritol mono-hydroxypentaacrylate (SR 399 from the Sartomer Co.) for the 6.0 grams of methylmethacrylate.

30 From this composition a gel coated reinforced polyester laminate was prepared in a manner similar to Example 4.

The resulting panel displayed a greater than 7H pencil hardness, could not be scratched with No. 00 steel wool, did not lose bond when subjected to the crosshatch - tape pull test and had  
35 gloss readings of 90 and 75, respectively, on the 60 and 20 degree Gardner scales.



CLAIMS

1. A process of making a laminated plastic article, the process comprising the steps of :
  - 5 A. Providing a mold having a surface corresponding to the article in negative relief ;
  - B. Spreading over at least a portion of the surface of the said mold a peroxide-curable gel coat composition comprising :
    - 10 1. An  $\alpha$ ,  $\beta$ -ethylenically unsaturated oligomer selected from the group consisting of unsaturated polyesters, and acrylated and methacrylated urethanes, epoxies, polyesters and polyethers ;
    2. A curing amount of a polyallylic crosslinker-initiator ; and
    - 15 3. A cure-rate promoting amount of a metallic salt drier ;
  - C. At least partially curing the gel coat composition ;
  - D. Spreading at least a partially uncured, plastic composition over the at least partially cured gel coat composition to form a laminate ;
  - 20 E. Curing the laminate to form the plastic article ; and
  - F. Removing the plastic article from the mold.
2. The process of Claim 1 in which the gel coat composition includes a copolymerizable  $\alpha$ ,  $\beta$ -ethylenically unsaturated monomer.
3. The process of Claim 2 in which the unsaturated oligomer and  
25 monomer, in combination, comprise at least 65 weight percent of the precured gel coat composition.
4. The process of Claim 3 in which the unsaturated monomer comprises less than 30 weight percent of the combination of unsaturated oligomer and monomer.
- 30 5. A process according to any of Claims 1 to 4, in which the polyallylic crosslinker-initiator comprises at least 5 weight percent of the precured gel coat composition.
6. A process according to any of Claims 1 to 5, in which the metallic salt drier comprises at least about 0.005 weight percent of  
35 the gel coat composition.

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7. The process of Claim 2 in which the monomer is selected from the group consisting of mono- and polyfunctional acrylic and methacrylic esters.
8. A process according to any of Claims 1 to 7, in which the  
5 polyallylic crosslinker-initiator is a polyallylglycidyl ether.
9. A process according to any of Claims 1 to 8, in which the gel coat composition is at least partially cured at a temperature between 20° and 95°C.
10. A process according to any of Claims 1 to 9, in which the gel coat composition includes at least one of a flow control agent, leveling agent, pigment, thixotropy agent or viscosity controller.
11. A process according to any of Claims 1 to 10, in which the gel coat composition is spread over the surface of the mold such that upon cure, the gel coat composition is less than about 1 mm in  
15 thickness.
12. A process according to any of Claims 1 to 11, in which the gel coat composition includes a non-polyallylic co-initiator.
13. A molded, laminated fiber-reinforced plastic article having a high initial gloss and extended gloss retention made by a process  
20 according to any of Claims 1 to 12.

## INTERNATIONAL SEARCH REP RT

International Application No.  
PCT/EP 93/02710A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B29C37/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	see page 1, line 9 - page 5, line 9	8
X	US,A,4 205 028 (W.H. BRUEGGEMANN ET AL) 27 May 1980	1-7, 10-13
Y	see column 2, line 57 - column 5, line 2	8,9
Y	EP,A,0 229 441 (GROUP LOTUS PLC) 22 July 1987	1-13
	see page 1, line 17 - line 50; claim 1	
Y	US,A,4 544 572 (T.C. SANDVIG ET AL) 1 October 1985	1-13
	see claims 1,3,12-15	
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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